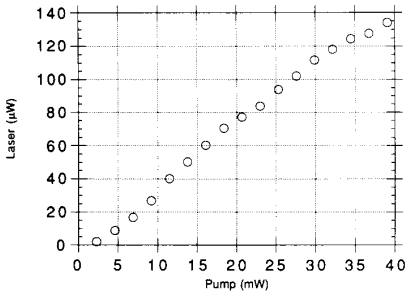

Fig. 5. Laser power versus pump power.

only a single longitudinal mode. Proper laser design also requires that the Bragg grating gain be accounted for when determining the single mode design regime and operating characteristics. This is required because the grating in an amplifying fiber will yield increased reflectivity over the same grating in a lossless fiber. Finally, this design analysis illustrates the need for the development of optimized high gain laser fibers since this performance can not be achieved in conventional low gain erbium amplifier fibers.

ACKNOWLEDGMENT

The authors would like to thank D. DiGiovanni at AT & T for providing the erbium doped fiber.

REFERENCES

[1] G. A. Ball, W. W. Morey, and W. H. Glenn, "Standing-wave monomode erbium fiber laser," *IEEE Photon. Technol. Lett.*, vol. 3, pp. 613–615, 1991.
[2] G. A. Ball and W. W. Morey, "Continuously tunable single-mode erbium fiber laser," *Opt. Lett.*, vol. 17, pp. 420–422, 1992.
[3] J. L. Zyskind, V. Mizrahi, D. J. DiGiovanni, and J. W. Sulhoff, "Short single frequency erbium doped fibre laser," *Electron. Lett.*, vol. 28, pp. 1543–1544, 1992.
[4] G. A. Ball and W. H. Glenn, "Design of a single-mode linear-cavity erbium fiber laser utilizing Bragg reflectors," *J. Lightwave Technol.*, vol. 10, 1992.
[5] D. K. W. Lam and B. K. Garside, "Characterization of single-mode optical filters," *Appl. Opt.*, vol. 20, pp. 440–445, 1981.

The Optical Second-Harmonic Generation from Porous Silicon

Kuang-Yao Lo and Juh Tzeng Lue

Abstract—**Second-harmonic generation from porous silicon with a magnitude of two orders greater than that from silicon crystalline wafers has been observed. The measured effective second-order nonlinear susceptibility $\chi^{(2)}_{ps.eff}$ for a p-type porous silicon is 1.96×10^{-7} esu which is estimated on the base of a bulk property rather than on quantum confinement owing to its large surface to volume ratio.**

I. INTRODUCTION

CANHAM [1] first demonstrated the visible photoluminescence from porous silicon (PS), after that most efforts have been focused on its photoluminescence mechanism. Brandt *et al.* [2] compared the optical property and the structure of anodically oxidized porous silicon with that of chemically synthesized siloxene and its related compounds showing that they have similar spectra. They hypothesized that visible light emission from PS depends on specific chemical bonding of silicon with hydrogen and/or oxygen atoms. The Fouries transform infrared-red (FTIR) spectra [3], [4] of PS indicate the existence of stretching modes of Si = 0 and Si-H bonds, suggesting the absorption or bonding of heteroatoms or molecules on the wall surface after electrochemical etching. The detection of optical second-harmonic generation (SHG) from PS is a sensitive method to probe the surface character. Some interesting properties of PS such as structure orientation, distribution of absorbed molecules, and the variation of chemical composition, can be determined by SHG. In this work, we attempt to elucidate the technique of SHG as a probe to the surface of PS.

The technique of surface SHG is based on the fact that a second-order process imposed by electric dipole is forbidden for media with crystallographic inversion symmetry. Consequently, the SH signal generated from the interface of a centrosymmetric conducting medium originates mostly from the electric quadrupole components within the selvedge region, with a minor part coming from the magnetic dipole term within the skin-depth region. Con-

Manuscript received December 22, 1992; revised March 5, 1992. This work was supported by the National Science Council of the Republic of China.

The authors are with the Department of Physics and the Department of Electrical Engineering, National Tsing Hua University, Hsin Chu, Taiwan, ROC.

IEEE Log Number 9209611.

sidering the large surface to volume ratio of PS with the adhesion of Si-O-H bonds on the wall surface, the pronounced second-order susceptibility of PS, which is denoted as $\chi_s^{(2)}$, is proposed to arise from the molecules on the porous surface. The second-harmonic intensity in the reflected direction is expressed by [6]

$$I(2\omega) = \frac{32\pi^3\omega^2 \sec^2\theta_{2\omega}}{c^3\epsilon(\omega)\epsilon^{1/2}(2\omega)}\left|\hat{e}_{2\omega}\cdot\chi_s^{(2)}:\hat{e}_\omega\hat{e}_\omega\right|^2 I^2(\omega) \quad (1)$$

where $\epsilon(\omega)$ and $\epsilon(2\omega)$ are the dielectric constants of the medium for the fundamental and SH field respectively; and $\hat{e}_\omega$ and $\hat{e}_{2\omega}$ are the propagating vectors of the pump and SH field with a proper calibration from the Fresnel factor, respectively.

If the fundamental wave is p-polarized in the xz plane, where z is normal to the surface, then the only nonvanishing components of the second order susceptibility are χ_{zzz}, χ_{zxx} and χ_{zxz}. The Fresnel factors for the normal coordinates are

$$L_{xx} = \frac{2\epsilon_\omega k_{2\omega}\cos\theta_{2\omega}}{\epsilon_{2\omega}k_\omega\cos\theta_\omega + \epsilon_\omega k_{2\omega}\cos\theta_{2\omega}}$$

$$L_{yy} = \frac{2k_\omega\cos\theta_\omega}{k_\omega\cos\theta_\omega + k_{2\omega}\cos\theta_{2\omega}}$$

and

$$L_{zz} = \frac{2\epsilon_\omega k_\omega\cos\theta_\omega}{k_\omega\epsilon_{2\omega}\cos\theta_\omega + \epsilon_\omega k_{2\omega}\cos\theta_{2\omega}} \quad (2)$$

where k_ω and $k_{2\omega}$ are the wavevectors of the fundamental and SH light, respectively. The refractive index $n_\Omega + jk_\Omega$ and the dielectric constant $\epsilon'_\Omega + j\epsilon''_\Omega$ for PS are presumed to be the same as that for silicon which at $\Omega = 1.06$ μm are 3.673 + oj and 13.49 + oj; and at $\Omega = 0.532$ μm are 4.150 + 0.044j, and 17.22 + 0.182j respectively. Subsequently, we can evaluate the propagating vector $\hat{e}^i_\Omega = L_{ii}\cdot\hat{E}_\Omega$, where $\hat{E}_\Omega$ is the unit vector of the electric field at frequency Ω.

The samples prepared in this experiment are described as follows. The unpolished sides of (111) and (100) p-type silicon wafers are coated with silver film by dc sputtering to yield a good ohmic contact. The PS layers are formed by anodizing these wafers in 48wt.% HF and 98wt.% C_2H_5OH solution under a constant current density of 50–110 mA/cm^2 at an etching time of 15 min. The photoluminescence of PS can be checked by exciting with the 514 nm line of an argon ion laser at room temperature and is shown in Fig. 1.

The experimental setup for the detection of SHG has been described elsewhere [7], [8]. The light source is a Coherent product Model 76-5 Q-switched and mode locked Nd:YAG Laser. In this experiment, the incident angle is selected at 45° in order to yield a larger signal and for easier arrangement of the position of the filters and photomultipliers. The measured maximum second-harmonic reflections coefficients for the (100) and (111) porous silicon are 2.45×10^{-19} cm^2/W and 8.04×10^{-20} cm^2/W, respectively which is almost two-orders of magnitude greater than that of silicon substrate (i.e., 2.50×10^{-21} cm^2/W). As the sample surface is continuously irradiated by the laser pulses for a duration longer than 30 s, the SH intensity sharply drops to the value of the basic silicon wafer. The decay rates of the SH reflectance for the (100) and (111) PS surface are shown in Figs. 2 and 3, respectively. The rapid decay of the SHG under the irradiation of a low laser pulse of 0.2 W irradiation is suggested to be due to the thermal breaking of the weak Si-O-H bonds which are crucial to the generation of SH light in PS. The intensity of SHG is recovered when one changes the position of irradiation spot.

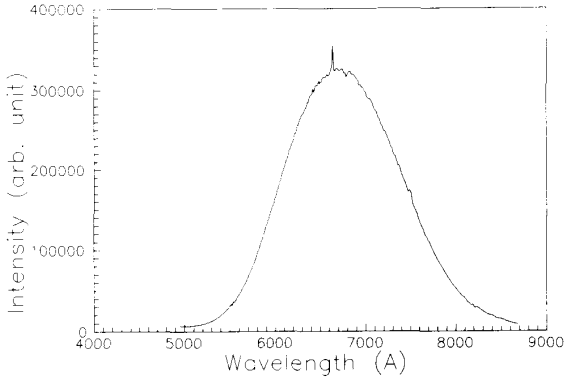

Fig. 1. The photoluminescence of PS pumped by 514.5 nm argon laser line.

Owing to the surface roughness of the porous silicon, the divergent factor of the beam profile due to surface scattering is about 4. This factor should be included in the estimation of the nonlinear susceptibility. Inplementing (1) and (2), we obtain the $\chi^{(2)}_{s,zzz}$ for the (100), (111) surfaces of PS and silicon substrate to be 1.968×10^{-7} esu, 1.114×10^{-7} esu and 9.84×10^{-9} esu respectively. The other two terms $\chi^{(2)}_{s,zxz}$ and $\chi^{(2)}_{s,zxx}$ are almost one or two orders of magnitude lower than their corresponding $\chi^{(2)}_{s,zzz}$ terms.

With regard to the origin of the SHG from PS, there are two possibilities. It can arise entirely from the surface, or the bulk. According to the bond charge model [9], [10], the ensemble average of the coordinates ξ in q orders is

$$\langle\xi^q\rangle_{\text{orb}} = \langle\phi_{ij}|\xi^q|\phi_{ij}\rangle = \frac{\lambda^2}{1+\lambda^2}\langle\phi_i|\xi^q|\phi_i\rangle + \frac{1}{1+\lambda^2}\langle\phi_j|\xi^q|\phi_j\rangle$$

$$\langle\xi^q\rangle = B_q\langle\xi^q\rangle_{\text{orb}} \quad (3)$$

where λ is the hybridization factor for the molecular orbits, and B_q is the orientation average factor. For silicon and oxygen molecular bonds, we have $\phi_{\text{Si}} = 1/2\phi_{3s} + \sqrt{3}/2\phi_{3p}$ and $\phi_O = \phi_{2p}$. Therefore,

$$\xi^3_{\xi\xi\xi} = -\left(\frac{3e^3N_s}{\hbar^2\omega_0^2}\right)\langle\xi^3\rangle \equiv N_s\langle\cos^3\theta\rangle\alpha^{(2)}_{\xi\xi\xi} \quad (4)$$

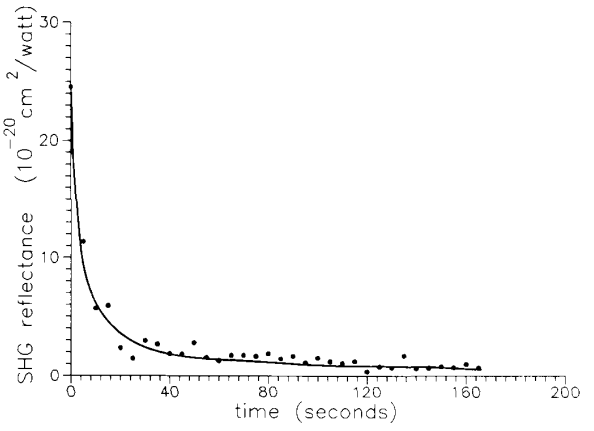

Fig. 2. The SH reflectance and decay rate for the (100) PS. The dots are the experimental values and the solid line is the best curve fitting.

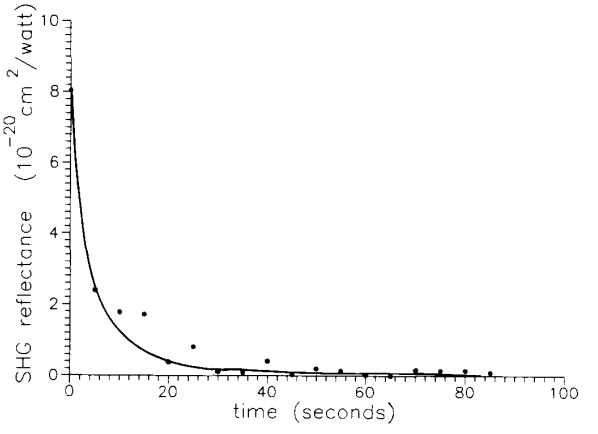

Fig. 3. The SH reflectance and decay rate for the (111) PS.

where N_s is the density of absorbed molecules per unit area on the surface in which the SiO molecules are considered to be like long rods aligned in the ξ axis which inclines with $\hat{z}$ by angle θ. The microscopic susceptibility estimated from the bond charge model is about 1.2×10^{-30} esu. Assuming a maximum value of $N_s \simeq 10^{16}/\text{cm}^2$, and with a $\theta \simeq 15°$, we can calculate the surface nonlinear susceptibility which is much smaller than the experimental results. The extraordinarily high $\chi^{(2)}_{zzz}$ for PS may be attributable to the high surface to volume ratio of the Si-O-H bonds [2], [11] absorbed on the well walls.

In conclusion, we have, for the first time, observed the SHG of PS which has an intensity of two orders of magnitude greater than its original silicon wafers. The SHG rapidly decays by the irradiation of laser pulses as is presumed to be due to the breaking of the Si-O-H bonds which are attached on the porous wall surface and are crucial to the anharmonic oscillations.

REFERENCES

[1] L. T. Canham, "Silicon guantum wire array fabrication by electrochemical and chemical dissolution of wafers," *Appl. Phys. Lett.*, vol. 57, pp. 1046–1048, 1990.

[2] M. S. Brandt, H. D. Fuchs, M. Stutzmann, J. Weber, and M. Cardona, "The origin of visible luminescence from porous silicon, a new interpretation," *Solid State Comm.*, vol. 81, pp. 307–311, 1992.

[3] T. Ito, H. Kiyama, T. Yasumatsu, H. Watabe, and A. Hiraki, "Role of hydrogen atom in anodized porous silicon," *Physica B*, vol. 170, pp. 535–539, 1991.

[4] Y. Kato, T. Ito, and A. Hiraki, "Initial oxidation process of anodized porous silicon with hydrogen atoms chemisorbed on the inner surface," *Jap. J. Appl. Phys.*, vol. 27, pp. 1406–1409, 1988.

[5] N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, "Optical second-harmonic generation in reflection from media with inversion symmetry," *Phys. Rev.*, vol. 174, pp. 813–822, 1988.

[6] Y. R. Shen, *The Principle of the Nonlinear Optics*. New York: Wiley, 1984, p. 25.

[7] C. C. Tzeng and J. T. Lue, "Optical second-harmonic generation of modulation doped $Ga_{0.8}Al_{0.2}As$ film grow by molecular beam epitaxy," *Solid State Comm.*, vol. 64, pp. 621–624, 1987.

[8] J. T. Lue and K. W. Mai, *IEEE Photon. Technol. Lett.*, vol. 5, Jan. 1993.

[9] S. S. Jha, and N. Bloembergen, "Nonlinear optical susceptibilities in group IV and III-V semiconductors," *Phys. Rev.*, vol. 171, pp. 891–898, 1968.

[10] J. C. Phillips, and J. A. van Vechten, "Nonlinear optical susceptibilities of covalent crystals," *Phys. Rev.*, vol. 183, pp. 709–711, 1969.

[11] K. Y. Lo, J. T. Lue, S. K. Ma, C. L. Chen and C. S. Chang, *Solid State Comm.*, vol. 85, 1993.